

Review Article

Manipulation of Energy Transfer Processes in Nanochannels

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The realisation of molecular assemblies featuring specific macroscopic properties is a prime example for the versatility of supramolecular organisation. Microporous materials such as zeolite L are well suited for the preparation of host-guest composites containing dyes, complexes, or clusters. This short tutorial focuses on the possibilities offered by zeolite L to study and influence Förster resonance energy transfer inside of its nanochannels. The highly organised host-guest materials can in turn be structured on a larger scale to form macroscopic patterns, making it possible to create large-scale structures from small, highly organised building blocks for novel optical applications.

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1. Introduction

Supramolecular organisation is a fruitful concept for the design of systems exhibiting specific macroscopic properties. Molecular sieves, such as zeolites, have been shown to be ideal host materials for the supramolecular organisation of dye molecules, complexes, or clusters. The inserted species usually exhibit an increased chemical and photochemical stability in the host matrix. Constraints imposed by the well-defined geometry of the host channels or cavities lead to a preferred spatial arrangement of the guests, thereby generating highly organised materials. Further functionalities can be added by assembling host-guest objects into well-defined macroscopic structures on various supports [1–18] and by promoting communication between guests and external species or devices [17–19]. The large variety in pore structure and morphologies provided by different types of molecular sieves offers many possibilities for the design of host-guest materials with specific properties [20]. Readers are referred to [21–23] for reviews on chromophores in porous silica and minerals. This tutorial will be focused on zeolite L, as it has proven to be an excellent host material for the organization of highly luminescent guest molecules [24–27]. The reasoning and methods presented here are, however, also valid for other host materials with similar properties. The tutorial will start with a description of the host material

and how guests are arranged inside of it. We will follow with a short theoretical background on Förster resonance energy transfer, for which we use the abbreviation FRET, illustrated with a case study. The last section will be devoted to an overview on how dye-zeolite materials can be arranged into larger patterns to form highly organized materials for novel optical applications.

2. Discussion

2.1. Supramolecular Organization of Guests inside of Zeolite L. Zeolite L crystals can be synthesised with different morphologies and sizes varying from of 30 nm up to about 10 000 nm, meaning that about 7 orders of magnitude in terms of volume can be covered [28–34]. Figure 1 depicts the structure and morphology of zeolite L. The primary building unit of the framework consists of TO_4 tetrahedrons where T represents either Al or Si. The secondary building unit, the cancrinite cage, is made up by 18 corner-sharing tetrahedrons. These cages are stacked into columns, which are then connected by means of oxygen bridges in the *a,b* plane to form a one-dimensional channel system running parallel to the crystals *c*-axis, exhibiting a hexagonal symmetry. The molar composition of zeolite L is $(\text{M}^+)_9[(\text{AlO}_2)_9(\text{SiO}_2)_{27}] \times n\text{H}_2\text{O}$, where M^+ are monovalent cations, compensating

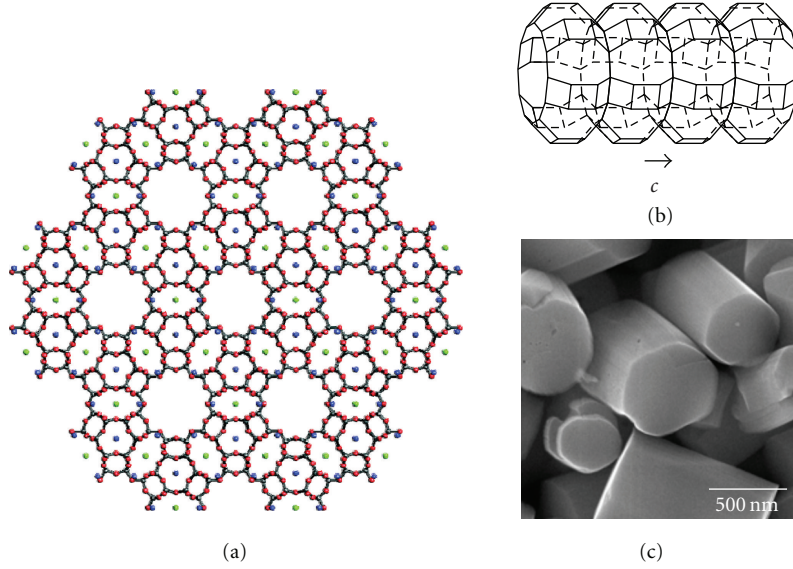


FIGURE 1: Zeolite L. (a) Top view of the structure of zeolite L illustrating its hexagonal framework. It shows a channel surrounded by six neighbouring channels. The centre-to-centre distance between two channels is 1.84 nm. (b) Side view of a channel that consists of 0.75 nm long unit cells with a Van der Waals opening of 0.71 nm at the smallest and 1.26 nm at the widest place. (c) SEM image of zeolite L crystals.

the negative charge resulting from the aluminium atoms. n is equal to 21 in fully hydrated materials, and to 16 for crystals equilibrated at about 22% relative humidity [35–38].

Zeolite L can be considered as consisting of a bunch of strictly parallel channels [19, 24–27, 39]. The channels have the smallest free diameter of about 0.71 nm, while the largest diameter inside is 1.26 nm. The centre-to-centre distance between two channels is 1.84 nm. Each zeolite L crystal consists of a large number of channels (n_{ch}) which can be estimated by

$$n_{\text{ch}} = 0.267(d_z)^2, \quad (1)$$

where d_z represents the diameter of the crystal in nm. For example, a crystal with a diameter of 600 nm features nearly 100 000 strictly parallel channels. The ratio of void space available in the channels with respect to the total crystal volume is about 0.26. An important consequence is that zeolite L allows through geometrical constraints the realization of extremely high concentrations of well-oriented molecules. Depending on their shape and size, the guests usually behave as monomers. A 30 nm by 30 nm crystal can take up to nearly 5000 dye molecules that occupy 2 unit cells; while a 60 nm by 60 nm crystal can host nearly 40 000 of the same guest type. The dye concentration of a dye-zeolite material $c(p)$ can be expressed as a function of the loading p as follows:

$$c(p) = 0.752 \frac{p}{n_s} \left(\frac{\text{mol}}{\text{L}} \right), \quad (2)$$

where n_s indicates the number of unit cells which form a site and can be occupied by one guest. The value of n_s is usually

an integer, but this must not necessarily be so. The loading, or occupation probability, p , is defined as follows:

$$p = \frac{\text{number of occupied sites}}{\text{total amount of sites}}. \quad (3)$$

Zeolite L is a versatile host material allowing for the design and preparation of a respectable variety of highly organized host-guest systems, as illustrated in Figure 2. It is the only currently available microporous material allowing the realization of the full range of organizational patterns presented here. The “cornerstones” in the development of these composite materials were the finding that dye-loaded crystals with different well defined domains can be prepared [40, 41], the invention of the stopcock principle [42, 43], the discovery of quasi 1D energy transfer [44], the preparation of unidirectional energy transfer material [17, 18, 45–47], and finding ways to create hybrid materials fully transparent in the visible range [48, 49]. The latter is important for spectroscopic investigations and some applications, since the small zeolite crystals exhibit considerable light scattering due to their size and refractive index between 1.4 and 1.5.

Guest species can be inserted into the channels of zeolite L either by ion exchange or by adsorption from the gas phase, depending on whether they are a charged or neutral species, respectively. The geometrical constraint imposed by the host leads to a highly ordered and well-defined arrangement of the guests inside the channels. Molecules that can pass the 0.71 nm pore openings of zeolite L are usually too large to overtake or stack with molecules already present in the channels. Thus one can create, by sequential insertion, materials with two or more defined domains, each containing only one type of guests. The geometrical confinement makes it also possible to reach very high concentrations of essentially monomeric dyes. Very small

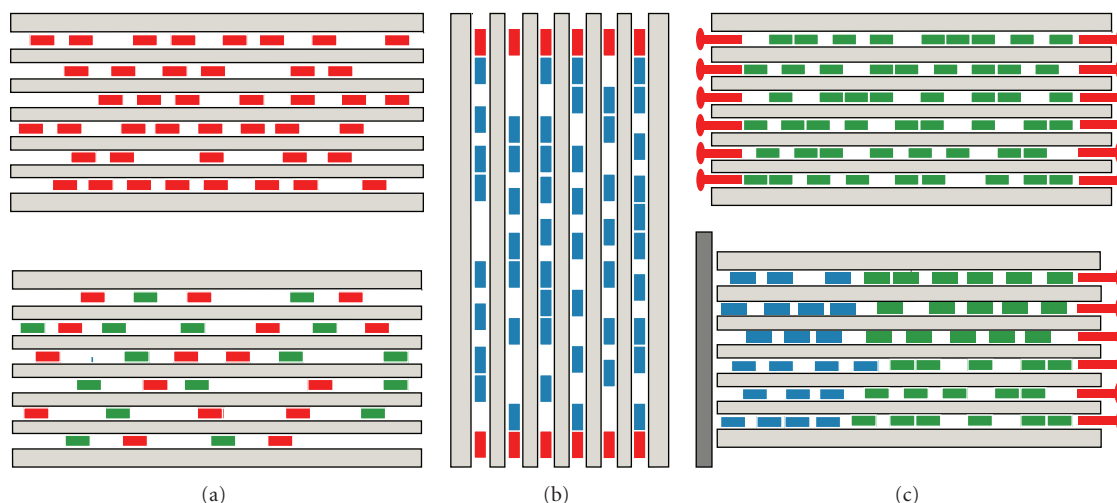


FIGURE 2: Schematic representations of supramolecularly organized dye-zeolite L systems. (a) *Single and mixed dye materials* are obtained by either loading zeolite crystals with one kind of dye (top) or by simultaneous insertion of different dye molecules (bottom). (b) *Antenna materials* can be prepared by the sequential insertion of different dyes. (c) *Stopcock-plugged antenna material* is obtained by modifying either bidirectional (top) or mono directional (bottom) antenna materials with specific closure molecules, called stopcocks.

molecules such as naphthalene can, however, form dimers inside of the channel system [50]. The structural formulae of dyes discussed in this work are summarised in Table 1.

Larger complexes can be prepared inside of the channel systems by means of a “ship-in-a-bottle” synthesis, a principle that was first developed by DeWild et al. in the early 80s of last century [51]. In a first step, the metal centres are introduced by means of ion exchange. The potential ligands can then diffuse into the channels where they will complex the metal centres. The reaction is easiest close to the channel entrances, as the access to the deeper lying metal ions is more difficult due to spatial restrictions. This principle has been successfully applied for the preparation of many different materials [52–56].

The channel ends of zeolite L can be modified by specific closure molecules, consisting typically of a head and a tail. Due to spatial restrictions, only the tail can pass the channel openings, while the head group is too bulky to fit through [42, 43]. Depending on their nature, these so-called *stopcock molecules* can be bound to the pore openings by either physisorption, electrostatical interaction, or by covalent bonding. As these molecules are only partially located inside the channels, they can be envisaged as mediators for interactions of species inside the crystals with outside entities or objects. Fluorescent stopcocks can be used to extract or inject electronic excitation energy into or from the zeolite L crystals by FRET [24–27, 42, 43, 57, 58]. Stopcock molecules can also prevent penetration of small molecules such as oxygen and water or hinder encapsulated dye molecules from leaving the channels [59].

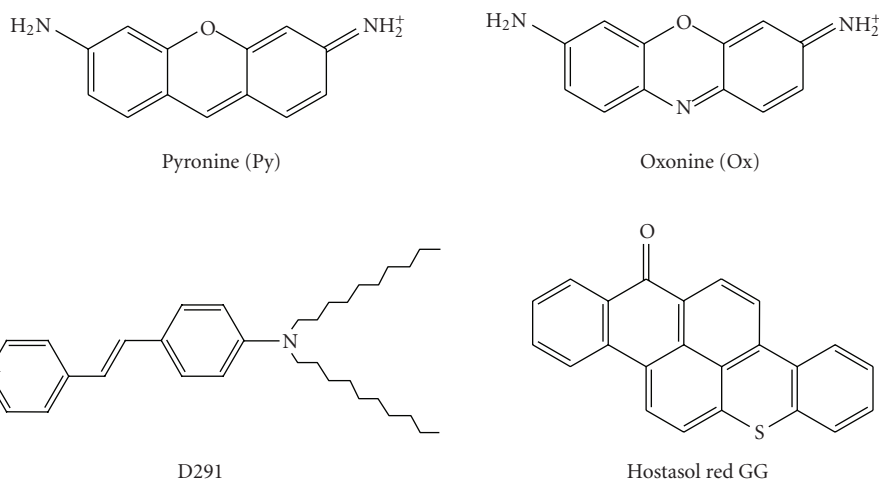
2.2. FRET Processes inside of Host-Guest Materials. This section will give a short overview on the theoretical background of FRET, followed by an experimental case study. Due to the geometrical properties outlined above, dye-zeolite L

composites are well suited for the study of FRET processes. The understanding of the FRET process is very advanced and goes back to the pioneering work of Förster [60–62]. A chromophore can be considered to consist of a backbone of positively charged nuclei surrounded by an electron cloud. When a photon is absorbed by the molecule, its energy is transformed into kinetic energy of one of these electrons. The oscillating electromagnetic field caused by the electrons rapid movement can interact with a neighbouring acceptor molecule A, as long as it bears states being in resonance with the excited state of the donor D^* . This radiationless electronic excitation energy transfer is solely due to the very weak near field interaction between excited configurations of the initial state ($D^* \cdots A_i$) and of the final state ($D \cdots A_i^*$). The Förster mechanism requires no orbital overlap between the donor and acceptor molecules. It should also be noted that this process involves no electron transfer from one species to the other. The donor D and the acceptor A can be either of the same type or they can be of different species. The rate constant k_{EnT} for the transfer from one electronic configuration to the other can be expressed as follows:

$$k_{\text{EnT}} = \text{TF} \frac{\kappa_{D^*A}^2}{n^4 R_{DA}^6} \frac{\phi_{D^*}}{\tau_{D^*}} J_{D^*A}, \quad (4)$$

where $\kappa_{D^*A}^2$ describes the relative orientation between the electronic transition dipole moments (ETDM) of donor and acceptor. This term can take values ranging from 0 to 4 for perpendicular or colinear arrangement of the ETDM, respectively. The centre-to-centre distance between the transition dipole moments is given by R_{DA} . Since the efficiency of the FRET process depends on the inverse sixth power of the intermolecular separation, it is useful over distances in the range of 1.5 nm to 10 nm. The terms ϕ_{D^*} and τ_{D^*} specify the quantum yield and lifetime of the donor in absence of acceptors. J_{D^*A} represents the overlap integral

TABLE 1: Summary of the structural formulae of dyes presented in this work.



between the acceptors absorption and the donors emission bands, thus taking into account the resonance condition. The environment of the donor-acceptor pair comes into play by the refractive index n . TF is a term that has been introduced to collect all constant terms from Theodor Försters original equation and has therefore the value [26, 27]

$$TF = \frac{9000 \ln(10)}{128\pi^5 N_L} \quad \text{or} \quad TF = 8.785 \cdot 10^{-25} \text{ mol.} \quad (5)$$

A nice case study of a FRET process is the mixed Py,Ox-zeolite L system [63]. The insertion kinetics of the strongly fluorescent dyes Py and Ox into zeolite L are very similar, providing a statistically homogeneous distribution of both dyes over the whole crystal. These dyes form an excellent donor acceptor pair, due to the large overlap ($J_{Py/Ox}$) between the Py fluorescence and the Ox absorption spectra as can be seen in Figure 3(a). The energy transfer process is illustrated by the photographic images seven fluorescent samples in Figure 3(b). Zeolite L crystals with an average length of 300 nm were used for preparation of all samples. The two references Py and Ox were loaded with a concentration of 5×10^{-3} M of Py or Ox, while the samples A to E were filled with a 1:1 mixture of both dyes. The concentrations for samples shown in Figure 3(a) are: A, $p = .0028$; B, $p = .0070$; C, $p = .0140$; D, $p = .0280$; E, $p = .0560$. The increasing dye concentration from A to E leads in turn to a decrease in the mean donor-acceptor distance. All samples were excited at 485 nm, where Py has a strong absorbance and Ox absorbs next to no light. Sample A exhibits mainly the green fluorescence of Py, indicating that energy transfer is insignificant. This is schematically shown by the donor-acceptor configuration on the left of the photograph. The low dye loading leads to large donor-acceptor distances. After selective excitation of the donor, its fluorescence intensity is dominant (green light). The energy transfer process to an acceptor is insignificant, and thus acceptor fluorescence (red light) is very weak. The yellow colour of sample B is due to a mixture of green and red fluorescence, meaning that energy transfer becomes significant in this case. The process becomes more and more important with increasing

concentration so that from sample C on, the red fluorescence stemming from Ox is dominant. The donor-acceptor scheme on the right of the photograph illustrates this for the case E. The high dye loading results in a short donor-acceptor distance, increasing the efficiency of the energy transfer process. As a result, the donor fluorescence is significantly quenched, while fluorescence from the acceptors is strong.

The same effect can be observed on the single crystal scale, by following the diffusion of the random dye mixture as a function of time [64]. The fluorescence microscopy images of a mixed Py,Ox-zeolite L sample given in Figure 3(c) illustrate this very nicely. The images were taken after loading the crystals for 20 minutes (1), 60 minutes (2), 470 minutes (3a, 3b), and 162 hours (4), respectively. For all images, Py was specifically excited, with the exception of 3b where Ox^+ was specifically excited. The samples with short equilibrium times exhibit an orange to yellow luminescence, due to the overlap of the green Py and red Ox emission, an indication for efficient FRET. After a diffusion time of 162 hours, the dyes are so far apart from each other that upon selective excitation of Py only green emission can be observed.

2.3. Organizing Host-Guest Materials on Larger Scale. A higher degree of supramolecular organization can be reached by arranging the dye-zeolite composites into larger structure. Such hierarchically organized structures, presenting successive ordering from the molecular up to macroscopic scale, are of great interest for nanotechnology due to the relationship between molecular arrangements and macroscopic properties [65, 66]. The organization of quantum sized particles, nanotubes, and microporous materials on different surfaces has been studied and used in science, technology, diagnostics, and medicine [67–76]. Size, shape, and surface composition of the objects but also the properties of the surface on which they should be organized play a decisive role and in some cases determine not only the quality of the self-assembly but also its macroscopic properties. Self-assembly strategies in the organization of matter make hierarchical ordering attractive by avoiding expansive techniques such

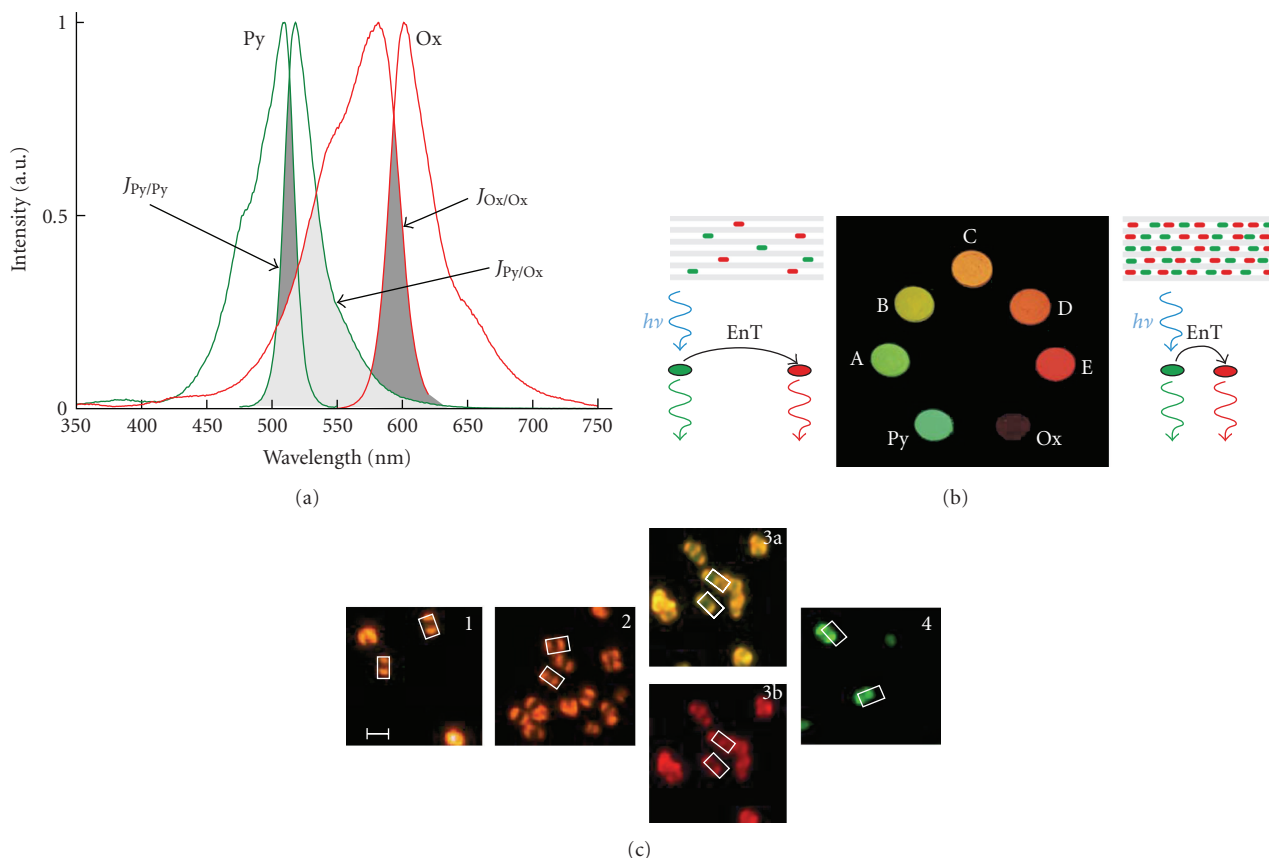


FIGURE 3: FRET case study on a mixed Py,Ox-zeolite L composite. (a) Excitation and fluorescence spectra of both dyes in zeolite L scaled to the same height at the maximum. The different overlap areas are indicated by grey shading. (b) Middle: photographic image of dye-loaded zeolite L layers upon monochromatic irradiation at 485 nm and observation through a 500 nm cut-off filter. The two samples indicated as P and Ox are references loaded with pure Py and Ox, respectively. Samples A to E contain a 1:1 mixture of Py and Ox with the following loading for each dye: A, $p_{1/2} = .0014$; B, $p_{1/2} = .0035$; C, $p_{1/2} = .007$; D, $p_{1/2} = .014$; E, $p_{1/2} = .028$. Left: Crystal and donor-acceptor pair describing the situation in sample A. Right: Crystal and donor-acceptor pair describing the situation in sample E [63]. (c) Fluorescence microscopy pictures, visualizing the diffusion of Ox to Py in zeolite L, taken after 20 minutes (1), 60 minutes (2), 470 minutes (3a, 3b), and 162 hours (4), respectively. Py was specifically excited, with the exception of 3b, where Ox was specifically excited. Two crystals of each image are framed. The scale given in 1 corresponds to a length of 1.5 μm [64].

as photolithography. An overview of hierarchically ordered materials that were created by self-assembly from dye-zeolite composites is given in Figure 4 [26, 27].

Hybrid polymer/dye-zeolite L materials with randomly oriented crystals, as shown in Figure 4(a), are obtained by dispersing surface modified zeolites in the precursor monomer followed by a specific polymerization procedure [48, 49]. Surface modification with alkoxysilane derivates improves the miscibility of the crystals with the organic monomers and even enabling copolymerization when an appropriate organic substituent is used. In this type of material, the usually strong light scattering of zeolite L can be suppressed by refractive index matching and avoidance of microphase separation.

Materials containing crystals oriented in a nematic phase, as shown in the sketch of Figure 4(b), can be obtained by using elastic polymers as substrate. After appropriate treatment of the polymer substrate such as stretching it with or without gentle heating, the crystals form the desired

nematic phase. The mechanical stretching force influences the zeolites and most will align along the pulling direction. The SEM and fluorescence microscopy images of Py-zeolite L embedded into a PVC polymer film shown in Figure 4(b) illustrate this well [48, 49].

Strategies based on the minimization of interfacial free energy for self-assembly have been applied to position small objects at the micrometric scale [81]. A novel approach towards micropatterning employing a surface tension was realized by Yunus et al. [78]. It was shown that dye-zeolite L crystals can be organized into hexagonal arrangement on a patterned polydimethylsiloxane (PDMS) surface as illustrated by the SEM and fluorescence microscopy images in Figure 4(c). The assembly process here is driven by surface tension interactions. This principle is a powerful tool for manipulations at the micrometer scale, allowing us to hierarchically organize molecular dyes on a macroscopic level.

Zeolite L crystals, with diameter around 700 nm and length in the range of 1 μm , have been successfully embedded

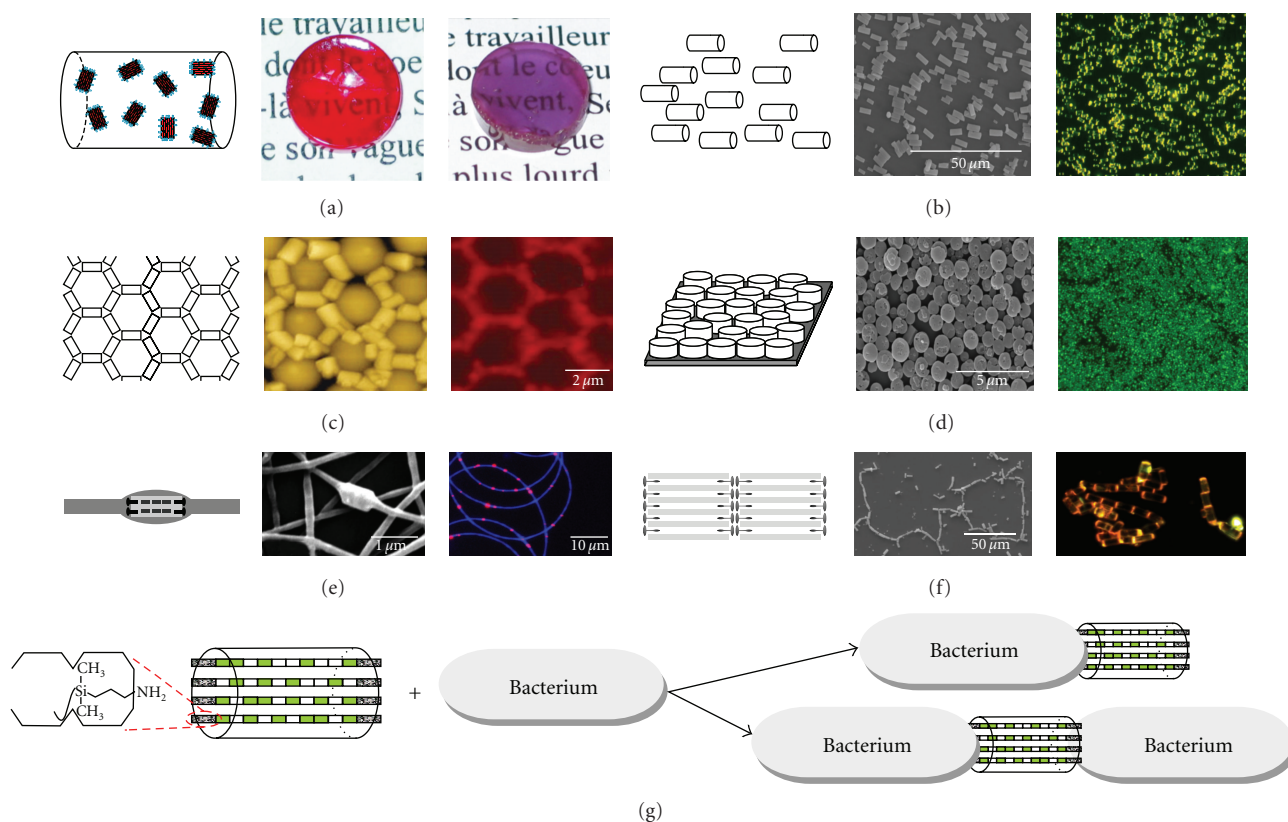


FIGURE 4: Summary of materials obtained by supramolecular organizations of zeolite L crystals. (a) Randomly oriented zeolite L crystals in a polymer. Photographic images of zeolite L-polymer hybrid materials prepared from crystals loaded with either red or violet dyes (Hostasol Red GG or Ox⁺, resp.) [48, 49]. (b) Nematic phase arrangement. Left: SEM and fluorescence microscopy image of Py⁺-zeolite L crystals aligned in a stretched PVC plastic film [77]. (c) Hexagonal arrangement. The dye-zeolite L crystals are organized by a surface-tension-driven self-assembly process on a PDMS/PS film (SEM and fluorescence microscopy image are shown) [78]. (d) Monolayers of standing zeolite L crystals. Left: SEM image of a monolayer. Right: fluorescence microscopy image of a monolayer loaded with Py [45–47]. (e) Nanofibers with embedded zeolite L. Left: SEM image of nanofiber with embedded zeolite L crystals. The crystals are oriented along the fiber axis. Right: Fluorescence image of a PEO/DDT nanofiber (blue emission) with embedded Ox-zeolite crystals (red sparks) [79]. (f) Chain-like assemblies of zeolite L crystals. Right: SEM image of zeolite crystals linked together by modifying the channel entrances with a cationic stopcock (D291) and corresponding fluorescence microscopy image [77]. (g) Assembly of zeolite L/bacterium in PBS buffer solution and self-assembly of two bacteria with functionalized 1-μm zeolite L as the junction [80].

into electrospun polymer fibers [79]. Electrospinning is a very efficient process for preparation of fibers with diameters ranging from the nano- to the micrometer scale [82, 83]. Polymer wires as thin as 150 nm are still able to enclose zeolites [84]. The crystals are aligned parallel to the fiber axis, as can be seen from the SEM image in Figure 4(e). Nanowires prepared by incorporating dye-loaded zeolites act as very bright, polarized light sources (Figure 4(e), left part) and are currently investigated for advanced nanophotonic applications.

Stopcock-plugged zeolite L crystals can be arranged into chain-like one-dimensional assemblies by exploiting coordinative interactions between the head groups of the stopper molecules, as illustrated in the scheme of Figure 4(f). The reversible nature of such coordinative bonds makes it possible to maximize the base-to-base interaction between crystals [85]. The chain-like arrangement of zeolite L crystals seen in the SEM image of Figure 4(f) is due to Van der Waals interactions between the long alkyl tails

of the stopcocks. The fluorescence microscopy image on the right part of Figure 4(f) shows a similar assembly of stopcock-plugged crystals. The luminescence concentration at the zeolite basal surfaces indicates the presence of the stopper molecules. Such microbarcode structures may be of interest for tagging or bio-imaging purposes [86, 87].

A recent breakthrough was realized by the attachment of dye-zeolite composites with amino-functionalized surfaces to living entities such as nonpathogenic *Escherichia coli* (*E. coli*) bacteria [80]. The situation schematically depicted in Figure 4(g) was investigated by means of optical and scanning electron microscopy. An interesting observation was that the crystals seem to always bind to one of the poles of *E. coli*. It was also possible to connect two bacteria together via a bridging, surface modified zeolite L crystal. The self-assembly of living systems with functional materials through chemically programmed construction opens up fascinating research fields.

3. Conclusion

The supramolecular organisation of molecules, complexes, or clusters inside the channels of zeolite L leads to host-guest composites with fascinating properties, a prime example being their use as artificial antenna materials. Further functionalities can be added by assembling such host-guest systems into well-defined macroscopic structures on various supports and by promoting communication between guests and external species or devices. The stopcock principle offers an elegant way to interface dye-loaded zeolite L crystals to other devices such as solar cells or even biological systems. Such materials are of interest in the development of novel optical devices such as luminescent probes, lenses, special mirrors, filters, polarisers, grids, optical storage devices, windows, and luminescent concentrators [26, 27, 88–90].

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